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BULLETIN No. 174-3

FIELD EVALUATION OF
ANAEROBIC DENITRIFICATION
IN SIMULATED DEEP PONDS

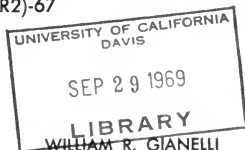
BIO-ENGINEERING ASPECTS OF
AGRICULTURAL DRAINAGE

U. S. Bureau of Reclamation
Contract No. 14-06-200-3389A
Federal Water Pollution Control Administration
Demonstration Grant WPD 143-01-(R2)-67

MAY 1969

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FOREWORD

In 1957, the State Legislature authorized the San Joaquin Valley Drainage Investigation. The purpose of this investigation is to resolve the agricultural waste water disposal problems of the San Joaquin Valley. As in most areas in which irrigated agriculture is practiced, the drainage problems have been handled on a local scale. The beginning of the Drainage Investigation indicated that drainage was finally being thought of as it should--as a problem for the whole basin, and not a problem of just the unfortunate few.

Several phases of the quality and treatment studies of the San Joaquin Valley Drainage Investigation are of such a nature that they merit special publication. For this reason a special series of bulletins, all with the same basic number--174, has been created under the general heading of "Bio-Engineering Aspects of Agricultural Drainage".

Bulletin 174-3, the third of the series, is a field evaluation of the anaerobic denitrification process in simulated deep ponds. The work done is part of the Interagency Nitrogen Removal Treatment Project, and was conducted at the Agricultural Waste Water Treatment Center near Firebaugh, California. The project was designed as an intermediate field step between the laboratory studies, described in the Appendix, and the pilot-scale field studies.

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April 8, 1969

ABSTRACT

This report contains the results of an interagency (California Department of Water Resources, Federal Water Pollution Control Administration, and U. S. Bureau of Reclamation) project to demonstrate the field effectiveness of the anaerobic pond denitrification process for removing nitrate-nitrogen from subsurface agricultural waste waters. The study was conducted between June 1 and December 31, 1967, at the Agricultural Waste Water Treatment Center near Firebaugh, California, using three-foot diameter concrete pipes to simulate deep ponds. In the anaerobic denitrification process, bacteria are provided with methanol as a carbon source and reduce the nitrate ion to nitrogen gas.

The results of the study indicate that the process may be able to reduce as much as 80 percent of the nitrate-nitrogen in agricultural drainage water at a detention time of five days. It is recommended that the Federal Water Pollution Control Administration initiate pilot scale studies to more accurately determine nitrogen removal efficiencies and the economics of the process.

CHAPTER I INTRODUCTION

This project was part of a joint study by the Department of Water Resources (DWR), Federal Water Pollution Control Administration (FWPCA), and U. S. Bureau of Reclamation (USBR) of methods of removing nitrate-nitrogen ($\text{NO}_3\text{-N}$) from subsurface agricultural waste water. The work was conducted at the Agricultural Waste Water Treatment Center located near Firebaugh, California between June 1 and December 31, 1967. The original impetus for the study resulted from plans to discharge tile drainage water, via the San Joaquin Master Drain, into the Sacramento-San Joaquin Delta near Antioch. The relatively high nitrate-nitrogen level predicted for the drain (approximately 20 milligrams/liter (mg/l) $\text{NO}_3\text{-N}$) has a potential for causing undesirable blooms of algae in the receiving waters. The studies at Firebaugh have been implemented to determine the economics of the nitrogen removal processes as compared to ocean discharge sites.

In the anaerobic denitrification process, an organic carbon source (in this case methanol) is added to the water to provide food for bacterial growth. In a suitable container where reaeration is restricted, the bacteria soon utilize the available dissolved oxygen and then reduce the nitrate ion to nitrogen gas. The reduction is a two-step process with the nitrite ion as an intermediate product. The results of preliminary laboratory studies of the denitrification process were submitted to the Department in June of 1966 by Dr. Perry L. McCarty, Professor of Sanitary Engineering at Stanford University. Included in his report was a preliminary economic evaluation of the use of anaerobic denitrification to remove nitrogen from agricultural waste waters in the proposed San Joaquin Master Drain. Dr. McCarty's report is presented in the Appendix.

The objectives of the study at Firebaugh were to evaluate the denitrification process under field conditions and to determine if the FWPCA should proceed with pilot-scale studies. In addition, the study was to provide general information on the effect of detention times and temperature on the efficiency of nitrogen removal.

At Firebaugh, denitrification is being investigated by two methods--deep ponds and filters. This report evaluates the deep pond process. Anaerobic denitrification in filters, to be reported elsewhere, occurs while water is passed through columns filled with a suitable matrix. The matrix (carbon, sand, gravel, etc.) provides a large surface area for bacterial growth so that the time required to remove the nitrogen can be substantially reduced. The basic process is the same in the two methods.

CHAPTER II METHODS AND MATERIALS

Pipes

Six reinforced concrete pipes, 12 feet in length by 3 feet in diameter, were used in this study to simulate deep ponds. The pipes were set vertically in the ground to a depth of approximately 7 feet and sand was piled around them to make a final covered depth of about 10 feet. The bottoms were sealed with plywood and fiberglass resin, which was covered with two inches of grout. To study the effect of depth, the pipes were filled with sand so that there were 3 pipes with 6 feet and 3 pipes with 8 feet of water depth. When one of the deeper pipes leaked, the sand was removed and the pipe resealed. This pipe was left with a water depth of 11 feet. Figure 1 schematically shows a concrete pipe installation.

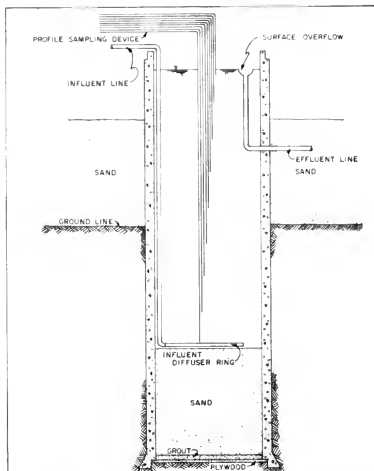


Fig. 1-SCHEMATIC OF A CONCRETE PIPE INSTALLATION

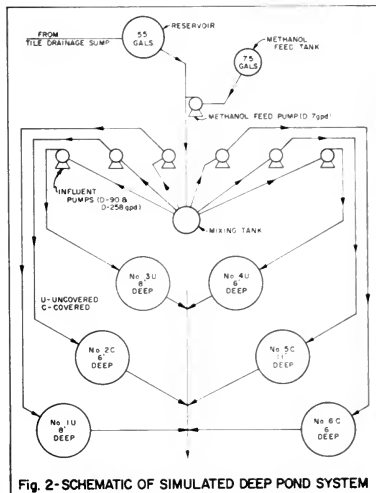


Fig. 2-SCHEMATIC OF SIMULATED DEEP POND SYSTEM

Pumping

Maintaining flows at desired quantities proved to be most troublesome and required an almost constant effort to keep the pumps operating as planned. Several pump setups were tried and discarded before a reasonably satisfactory installation was obtained. Much of the difficulty resulted from the growth of bacteria in feed lines, check valves, pump heads, etc. This growth, along with inherent mechanical variation in the pumps, made it difficult to maintain flows at the desired levels.

Figure 2 is a schematic diagram of the final simulated deep pond system. Five variable capacity pumps were used in the system. One with a capacity of 0 to 7 gallons per day (GPD) for the methanol feed pump, two with capacities of 0 to 90 GPD and two with capacities of 0 to 258 GPD for delivering water to the pipes. The two smaller capacity pumps were diaphragm pumps and were used to feed one pipe each. The two larger capacity pumps are twin-head, piston-type pumps and were used to feed four pipes. The flow path of water through the system was: the tile drainage water was pumped from the agricultural sump to a 55-gallon polyvinyl chloride (PVC) reservoir. The water flowed from the reservoir to a mixing tank. The methanol feed solution, which was prepared daily in a 7.5-gallon container, was injected into the water line just before the mixing tank. The mixed water-methanol solution was pumped to the six pipes, at distances of from 5 to 15 feet through 5/16" plastic tubing. The water-methanol solution was discharged near the bottom of the simulated deep pond through a two-foot diameter plastic diffuser ring. The effluent left the pipe through a surface flow which maintained water levels about four inches below the top of the pipe.

Sampling

Influent samples were obtained Monday through Friday, usually between 0800-0900, from the feed line just before the water entered the pipes. Effluent samples were obtained at the same time from the surface overflow discharge line. Nitrate-nitrogen levels for the tile drainage water were determined daily from samples taken at the sump.

Depth samples were obtained from a sampling device placed near the center of the pipe. This sampler consisted of a series of plastic tubes in a two-inch PVC pipe arranged so that a sample could be obtained at one-foot intervals throughout the water column. These depth samples were used to determine vertical profiles of dissolved oxygen, nitrate, methanol, and temperature.

Flow rates were normally determined daily by measuring the time required to fill a 500 milliliter volumetric flask. Occasionally the volume of effluent from one or more of the pipes was measured for a four-hour period to determine the accuracy of the flask measurements. Flow rates determined in this way were always in good agreement (within 1 to 5%) of the flows obtained by the shorter method.

Chemical Analyses

Chemical analyses were conducted according to the schedule shown in Table 1. Additional analyses, mainly depth profile of nitrate, nitrite, and methanol, were conducted as required.

TABLE 1
CHEMICAL ANALYSIS SCHEDULE

Constituent:	Frequency	: Number : of : Pipes : Sampled	: Source : of : Sample	: Method of Analysis
NO ₃ -N	Daily	6	(Influent & Effluent)	Brucine
NO ₂ -N	Twice-weekly	6	(Influent & Effluent)	Diazotination
NH ₃ -N	Once-weekly	2	Effluent	Kjeldahl-distillation
Organic N	Once-weekly	2	Effluent	Kjeldahl-distillation
Dissolved Oxygen	Once-weekly	6	(Influent, Profile, & Effluent)	Azide Modification-Winkler
Methanol	Three times weekly	6	(Influent & Effluent)	See description below

With the exception of the methanol test, all of the analyses were conducted according to the methods outlined in the 12th edition of "Standard Methods

for the Examination of Water and Waste Water". The methanol analysis was modified from a method for determining methanol vapor in air, described in a pamphlet obtained from the Chemical Solvents Corporation in Agnew, California. In this test, methanol was first reduced to formaldehyde, a colored compound was then formed and the light absorption was measured at 570 millimicrons with a Beckman Model B spectrophotometer. Concentrations were then estimated by comparison with the absorption of a known standard. This procedure appeared to give reliable results at higher concentrations of methanol (above 20 mg/l) but unknown interferences in the drain water made readings of less than 20 mg/l of doubtful validity. The Department's Bryte laboratory is currently working on a comparison of the results of this method with those obtained with a gas chromatograph. When the results of this comparison are available, methanol utilization can be evaluated more accurately.

Methanol (Carbon) Requirement

The methanol used is a commercially available, synthetically produced compound with a minimum purity of 99.85 percent. Cost of the compound varies from \$0.30 to \$1.65 per gallon, depending on the quantities purchased. The amount of methanol required to reduce a specified quantity of nitrate was calculated by the following equation (from Dr. McCarty's report):

$$\text{Methanol required (mg/l)} = \frac{3.85 \times (\text{NO}_3\text{-N, in mg/l)} + 1.5 \times (\text{dissolved oxygen, in oxygen equivalent of methanol})}{1.5}$$

The oxygen equivalent of methanol is 1.5. For a $\text{NO}_3\text{-N}$ concentration of 20 mg/l and dissolved oxygen of 7 mg/l the results are:

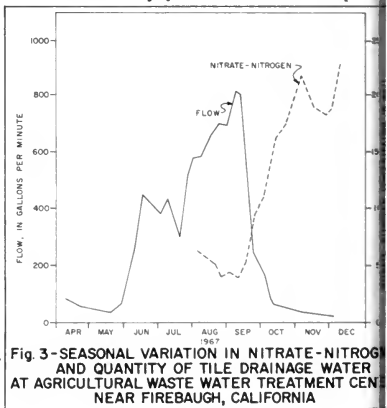
$$\text{Methanol (mg/l)} = \frac{(3.85) (20) + (1.5) (7)}{1.5} = 58.3 \text{ mg/l}$$

Bacterial Seeding

Each of the pipes was initially seeded with one liter of sludge from the Fresno sewage treatment plant's digester. Natural seeding would have been adequate but probably would have required more time to reach the population levels required to remove the nitrate.

Tile Drainage Water

The concentrations of constituents in subsurface tile drainage water depends on the agricultural materials and practices used on the land drained. During the past two summers, rice, (which requires 3-4 months flooding) has been grown on a portion of the land drained. Figure 3 contains graphs of flow and nitrate-nitrogen in Alamitos sump during the months of April through November, 1967. Flooding of the rice began about the first of June and was stopped during the first week in September. The concentration of nitrate-nitrogen decreased with increasing drain flow down to a minimum of about 3.8 mg/l near the first of September.



In Table 2, two mineral analyses of the tile drainage water are listed, one analysis before the rice was flooded, and a second, about one month after the water had been applied. The flow on May 2 was approximately 50 gallons per minute (gpm), and on July 14 was about 450 gpm.

TABLE 2

CONCENTRATION OF MINERAL CONSTITUENTS IN WATER FROM TILE DRAIN SUMP
AT AGRICULTURAL WASTE WATER TREATMENT CENTER NEAR FIREBAUGH
(in mg/l)

Constituent	Date	
	5-2-67	7-14-67
Calcium	373	194
Magnesium	190	106
Sodium	1390	875
Potassium	5.4	4.1
Carbonate	29	0
Bicarbonate	247	373
Sulfate	3600	2070
Chloride	559	304
Nitrate-Nitrogen	17.6	9
Hardness	1710	921
Total Dissolved Solids	6590	3950
Boron	14	9.3

The nitrate-nitrogen dropped to below 4 mg/l during the summer.

To make the results of the study more applicable to future work, nitrogen was added to the water in the form of sodium nitrate (NaNO_3) to give a total $\text{NO}_3\text{-N}$ concentration of approximately 20 mg/l. The concentration of nitrate in the influent was measured and adjusted daily as required.

CHAPTER III RESULTS

As shown in Table 1, chemical analyses of all forms in the nitrogen series were not conducted daily. However, to evaluate the percentage of nitrogen removed, all forms should be known at least approximately. Concentrations of nitrite, ammonia, and organic nitrogen for those days when no analyses were conducted were obtained by interpolating between known values. In most instances the day-to-day variation in concentration was low enough to make this approach valid. The problem of estimating the amount of nitrogen removed was further complicated by the rate at which water moved through the pipes. Because influent nitrogen varied from day to day, it is incorrect to use influent and effluent data for the same day to estimate removal efficiency--this neglects the residence time of the water in the pipe. This problem was at least partially solved by determining a moving three-day average of the influent nitrogen data (one day plus the two previous days). The average influent value was then used to calculate the amount of nitrogen removed.

Although the pipes were initially seeded on June 1, 1967, the data for the first three months are not used in this report. From June 1 through August 15, the pipes were on a batch feed basis with detention times of 10-20 days. On August 15 the feed pumps were put into operation but approximately two weeks were required to eliminate some of the mechanical problems and revise the pump system.

During the period when the pipes were on a batch-feed basis, the water in the uncovered pipes remained aerobic, as shown in Table 3, probably because of the photosynthetic production of oxygen. Because the bacteria in the system seem to be facultative (can grow in an aerobic or anaerobic environment) and utilize dissolved oxygen when available, nitrogen removal is reduced. To determine the extent to which oxygen produced by algae affected anaerobic denitrification, three of the pipes were covered on August 11 with a black polyethylene plastic to stop algal growth. In the following discussion covered pipes are denoted by a C following the number (e.g. 2C) and uncovered pipes by a U (e.g. 1U).

TABLE 3
DISSOLVED OXYGEN PROFILES (in mg/l) FOR PIPES
1U, 2C, 3U, 4U, ON SEPTEMBER 8, 1967, 1000-1100 HOURS

Depth From Surface In Feet	PIPE			
	:	:	:	:
	1U	3U	4U	2C
0	5.0	6.5	10.4	0.1
1	2.8	3.6	13.9	0.0
2	1.2	3.4	8.3	0.0
3	1.0	2.3	4.9	0.0
4	0.7	2.4	5.0	0.0
5	0.6	2.2	4.5	0.0
6	0.5	2.3	3.9	0.0
7	0.4	2.1		
8	0.5	1.5		

The plastic was later replaced with permanent, light-tight plywood covers. The pipes were then considered as three open containers which simulated natural field conditions and corresponding covered pipes serving as controls. Pipes 1U and 2C were left at theoretical detention times of eight days throughout the study to demonstrate the effect of algal growth, temperature, etc., without the additional variable of detention time to consider. Detention times were varied in the other two pairs 3U-5C and 4U-6C to study the effect of this variable, as well as those mentioned above.

Detention Time Dye Study

Theoretical hydraulic detention times were normally calculated from influent flow rates but these calculations neglected possible short-circuiting and stagnant zones. To determine if the calculated detention times were representative of the actual hydraulic regimes in the pipes, one milliliter slugs of Rhodamine B dye were injected into pipes 1U and 2C, which were both at a theoretical detention time of eight days, and the change of fluorescence with time was measured in effluent samples. These values are plotted in Figure 4, along with calculated values for a completely mixed container with an eight-day detention time.

A comparison of the results of the two injections shows that the movement of water was not the same for both pipes. Dye appeared in the effluent of both pipes within a short time after injection but at much lower concentrations in the covered pipe. In pipe 1U a peak was reached within 30 minutes after injection. The dye concentration then decreased for several hours after which it increased to a maximum about 22 hours after the injection. In pipe 2C the values increased gradually, reaching a maximum after about 22 hours. The general shape of the curve for pipe 1U was much more uneven than for the covered pipe, indicating that more short-circuiting and larger stagnant areas are present in pipe 1U than in pipe 2C. The difference between the two containers may have been the result of wind action or direct heating of the water by sun in pipe 1U.

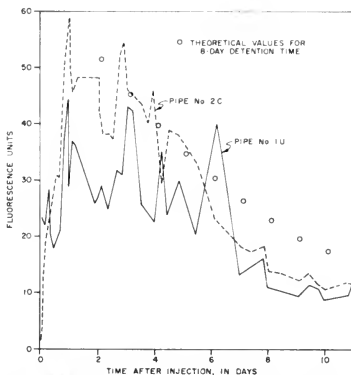


Fig. 4- CONCENTRATION OF DYE IN PIPE EFFLUENT

In later sections of this report, theoretical detention times are based on the total column volume divided by influent flow rates rather than true hydraulic detention times. Based on the dye study, this assumption may be valid for closed pipes but may not be entirely true for the open pipes.

Dissolved Oxygen

On September 22 and 23, 1967, a twenty-four hour study was conducted to determine the diurnal variation in dissolved oxygen concentration. Concentrations at the surface, four-foot depth, and eight-foot depth in pipes 1U and 3U are plotted in Figure 5. The dissolved oxygen at the surface reached maxima at about 1600 hours; in both pipes, values were considerably above the saturation value of approximately 8 mg/l. During the early morning hours, the concentration at the surface dropped to 5 mg/l in both pipes. The oxygen levels at the four-foot depth remained relatively constant at 4-5 mg/l during the twenty-four hours. The concentrations in the samples from the eight-foot depth, about two to four inches from the bottom, were always above zero but less than one mg/l in both pipes.

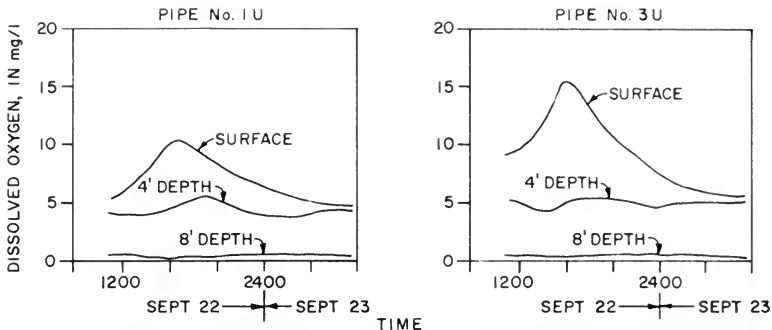


Fig. 5-DIURNAL VARIATION IN DISSOLVED OXYGEN AT VARIOUS DEPTHS IN PIPES 1U & 3U ON SEPT. 22 & 23, 1967

Weekly dissolved oxygen profiles from all of the pipes showed that, after September 29, 1967, the concentration rarely exceeded one mg/l at any depth in the open pipes. This may have been the result of the more reliable methanol feed system with probable increased bacterial populations. The larger biomass of bacteria may have inhibited algal growth by rapid removal of nitrogen or perhaps utilized the photosynthetic oxygen almost instantaneously.

Effect of Algal Growth

The adverse effect of oxygen produced by algal growth on nitrogen removal can be most easily seen in a plot of data from pipes 1U and 2C where the detention time remained at 8 days for the four-month period (Figure 6). During the entire period the bacteria in pipe 2C consistently removed about

25 percent more nitrogen than the bacterial population in 1U. The exception about the end of September was noted in all of the covered pipes during this period and may have been caused by insufficient methanol in the influent.

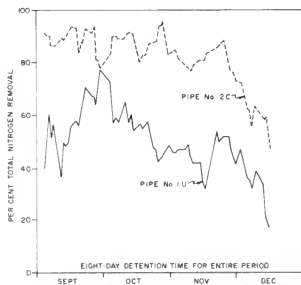


Fig. 6-EFFICIENCY OF TOTAL NITROGEN REMOVAL FOR PIPES 1U AND 2C

In the other two pairs of pipes (3U-5C and 4U-6C), Figures 7 & 8, percentages of nitrogen removed was again lower in the uncovered pipes than in covered pipes. The average difference in nitrogen removal was in the same general range as in 1U and 2C. In these two pairs, interpretation of the data was complicated by changes in detention time.

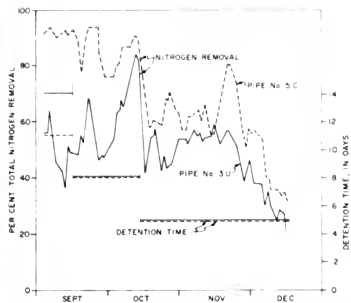


Fig. 7-EFFICIENCY OF TOTAL NITROGEN REMOVAL FOR PIPES 3U AND 5C

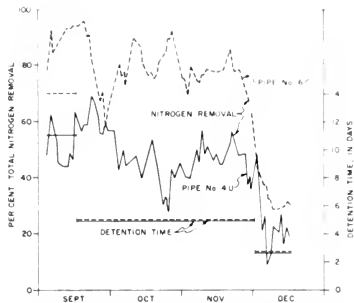


Fig. 8-EFFICIENCY OF TOTAL NITROGEN REMOVAL FOR PIPES 4U AND 6C

Effect of Temperature

The data in Table 4 can be used to reach some general conclusions concerning temperature effects on the ability of bacteria to reduce the nitrate ion to nitrogen gas. The average air temperatures were obtained from the weather bureau in Fresno, and the average water temperature from weekly temperature profiles. The temperature of the water in the tile drainage sump remained relatively constant at 59-63° F during the four months.

The temperature effect is best illustrated by the data from pipes 1U and 2C where detention time remained constant during the study period. In both of the pipes removal efficiencies were reasonably consistent during September and October. In November, nitrogen removal remained about the same in the covered pipe, but decreased in the open pipe. December removal efficiencies in both pipes were considerably lower than previous months. Where comparative data are available in the other pipes, the same pattern is evident, i.e., little temperature effect during September, October, and November with a sharp decrease during the month of December. The data from this study and the concurrent work on column anaerobic denitrification indicates that 60° F may be a lower limit for efficient operation on the system.

Effect of Detention Time

Dr. McCarty tested detention times of 10, 20, and 30 days on a fill and draw basis. In his preliminary study of denitrification, he found that 90 percent of the nitrogen was removed in 10 days and concluded that this detention time could be used in field studies. In this study, detention times from 2.7 to 14 days were used in an attempt to determine the minimum detention time which would provide 90 percent nitrogen removal.

The nitrogen removal data presented in Figures 6 through 8 are summarized in Table 4. Some generalizations can be made about the effect of detention time on nitrogen removal in simulated deep ponds. Looking first at the data from the covered ponds for September, October and November, it appears that approximately 90 percent removal of the influent nitrogen can be expected at 10 days or greater detention time, and 80 to 90 percent removal should be possible at 8 days detention time. At 5 days the data are somewhat conflicting in that approximately 80 percent of the nitrogen was removed in pipe 6C and only about 65 percent in pipe 5C. The only apparent physical difference between the two pipes was water depth--number 5C was 11 feet deep and number 6C was 6 feet deep. Because of the cold weather during December, no reliable estimate of removal efficiency at a detention time of 2.7 days can be made.

TABLE 4

COMPARISON OF AVERAGE PERCENT NITROGEN REMOVED, DETENTION TIME, AND AVERAGE MONTHLY AIR AND WATER TEMPERATURE

MONTH	AVERAGE MONTHLY TEMPERATURE OF AIR/WATER °F	PIPE NUMBER											
		1U		2C		3U		4U		5C		6C	
		a ^{1/}	b ^{2/}	a	b	a	b	a	b	a	b	a	b
SEPTEMBER	77/76	8	59	8	83	14	50	11	52	11	92	14	89
					8	62		60	8	86		79	
OCTOBER	66/67		62		88		49	5	45		64	5	82
NOVEMBER	57/60		45		81	5	53		47	5	63		75
DECEMBER	42/50		27		54		26	2.7	18		37	2.7	31

^{1/} a = Detention Time, in days^{2/} b = Average Percent Nitrogen Removed

Nitrogen removal in the open pipes seemed to be almost independent of detention time. Data from the three pipes 1U, 3U and 4U generally indicate that 50-60 percent nitrogen can be removed at detention times of from 5 to 14 days.

CHAPTER IV. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The field evaluation of anaerobic denitrification in simulated deep ponds was undertaken by the Department of Water Resources as part of the Interagency Nitrogen Removal Treatment Studies--an integrated cooperative effort of the Department, the Federal Water Pollution Control Administration and the U.S. Bureau of Reclamation. The field evaluation was conducted at the Interagency Agricultural Waste Water Treatment Center near Firebaugh, California. The objectives of the study were to evaluate the process under San Joaquin Valley field conditions and determine if pilot scale studies of the process by the FWPCA were justified.

The study was conducted between June 1 and December 31, 1967. Essentially work done during June, July and August produced a reliable operating system and an understanding of the process--with little meaningful data. Work done during the months of September through December produced the data from which the conclusions of this report are drawn.

The data obtained indicate that anaerobic denitrification can be an effective means of removing nitrate-nitrogen from subsurface agricultural waste waters.

In covered ponds, nitrogen removal efficiencies of 90 percent at about 10 days' detention time, or 80 percent at about 5 days' detention time, may be possible. These removal efficiencies probably can be achieved during the seven months of April through October which correspond with the estimated peak flow months of drainage facilities in the San Joaquin Valley.

The data indicate that lower winter temperatures reduce nitrogen removal efficiencies. It may be possible to achieve higher removal efficiencies by lengthening the detention times. Estimated winter drainage flows will range between 1/5 and 1/3 of the high summer flows.

The data obtained indicate that removal efficiencies in uncovered ponds probably will not exceed 50 to 60 percent. Nitrogen removal efficiencies in the uncovered pipes used in this study generally remained 25 to 35 percent lower than the covered pipes. In full-sized ponds the difference probably will be even greater due to the effects of surface reaeration, wind mixing, and possibly turnover. It may be possible to offset the lower removal efficiencies in uncovered ponds by providing additional organic carbon.

RECOMMENDATIONS: IT IS RECOMMENDED THAT THE FEDERAL WATER POLLUTION CONTROL ADMINISTRATION PROCEED WITH PILOT SCALE STUDIES OF POND DENITRIFICATION AS PART OF THE INTERAGENCY NITROGEN REMOVAL TREATMENT WORK.

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APPENDIX

FEASIBILITY OF THE DENITRIFICATION PROCESS FOR REMOVAL OF NITRATE NITROGEN FROM AGRICULTURAL DRAINAGE WATERS

Consultants Report

by

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Professor of Sanitary Engineering, Stanford University

June 30, 1966

ENGINEERING EVALUATION OF DENITRIFICATION PROCESS

Introduction and Summary

The purpose of the proposed San Joaquin Valley Master Drain is to collect low quality agricultural drainage water from the south San Joaquin Valley and to convey it to the easterly reaches of the San Francisco Bay system. Concern has been expressed over the possible detrimental effect this drainage water may have on the San Francisco Bay waters. Projected estimates of the chemical quality of the drainage water indicate that it will be highly saline and will also contain some pesticides and a relatively high concentration of nitrate nitrogen, a fertilizing compound. It appears that the most justifiable concern has been over the high concentration of nitrate nitrogen which could possibly stimulate undesirable growth of aquatic plants in the receiving waters. This report describes the results of a laboratory and engineering study made to evaluate the feasibility of the biological denitrification treatment process for removal of the nitrate nitrogen from the drainage waters.

The results of this study have indicated that approximately 90 percent of the fertilizing nitrogen can be removed by the denitrification process. This process is relatively simple. An organic chemical is added to the drainage water. The water is then stored for approximately 10 days in an open reservoir. Following this, the water is aerated and discharged to the receiving water. The unwanted nitrogen is lost as a gas and there are no waste products created which may require separate disposal. The treated water has a slight turbidity caused by the microorganisms which bring about the denitrification, but this will not be harmful to the receiving waters.

The estimated cost of this process is approximately \$27 per million gallons. The capital cost is very low and the major operating cost is for the added organic chemical (\$23.20 per million gallons for the methanol used in this study). It is highly likely that this chemical cost could be significantly reduced if an organic waste product were used, rather than the commercial compound upon which this estimate was made.

The denitrification process is attractive because of its simplicity, low capital cost, and effectiveness. It is recommended that a field scale study of this process be instigated to test the suggested design and operating procedures. It is also recommended that a study be made of possible organic waste products available for use which may further improve the economics of this process.

Principles of Denitrification

In the denitrification process, use is made of microorganisms which, in the absence of oxygen, convert nitrate nitrogen, a fertilizing element, to nitrogen gas, a harmless material which makes up 78 percent of the earth's atmosphere. This they can do only when supplied with an appropriate quantity of organic material which serves as an energy source and allows the microorganisms to carry out denitrification while they are reproducing and growing. A variety of organic materials ranging from pure commercial compounds to mixed organic wastes can serve this purpose. The microorganisms which bring about denitrification are the common "facultative" bacteria which are present in large numbers in the soil.

Denitrification is a two-stage process. In the first stage, nitrate nitrogen is reduced to nitrite nitrogen, another fertilizing element. In the second stage, the nitrite nitrogen is reduced to the desired end product, nitrogen gas. The two stage nature of denitrification is important to understand. If only one-half of the organic material required for denitrification is added, only the first stage reduction may occur and no effective nitrogen removal may be achieved. For this reason, the total required quantity of organic material must be added for effective denitrification. If only partial nitrogen removal is desired, then this is best accomplished by split treatment in which a portion of the waste is given full treatment and the other portion is not treated at all. The two portions are then blended to produce a partially treated water.

The quantity of organic chemical which must be added to agricultural drainage water for efficient denitrification to occur is dependent upon the quantity of nitrate nitrogen in the water and the initial dissolved oxygen concentration of the water as discussed in the "laboratory evaluation of denitrification process" portion of this report. In equation form, this quantity can be expressed as follows:

$$O_r = 3.85 (\text{NO}_3\text{-N}) + 1.5 (\text{DO}) \quad \text{--- (A-1)}$$

where O_r is the oxygen equivalent of the organic material required for denitrification, $\text{NO}_3\text{-N}$ is the nitrate nitrogen concentration and DO is the dissolved oxygen concentration in the drainage water. All quantities are expressed in milligrams per liter (mg/l). The oxygen equivalent, cost, and quantity of various organic chemicals which might be used for removal of the 21 mg/l of nitrate nitrogen estimated for the future San Joaquin Valley agricultural drainage water are listed in Table A-1. Of the chemicals considered, both methanol and acetone are the most economical. The experimental study described in the appendix indicated that for additional reasons, methanol is the best of the two chemicals for use in the denitrification process.

Proposed Treatment Process

A diagram of the proposed process for denitrification of agricultural drainage water is shown in Figure A-1. The required quantity of organic chemical is continuously fed and mixed with the drainage water. This mixture is continuously discharged to a relatively long and narrow reservoir with a depth of about 20 feet. Denitrification occurs as the mixture flows through the reservoir which should be sufficient in size to provide a theoretical detention

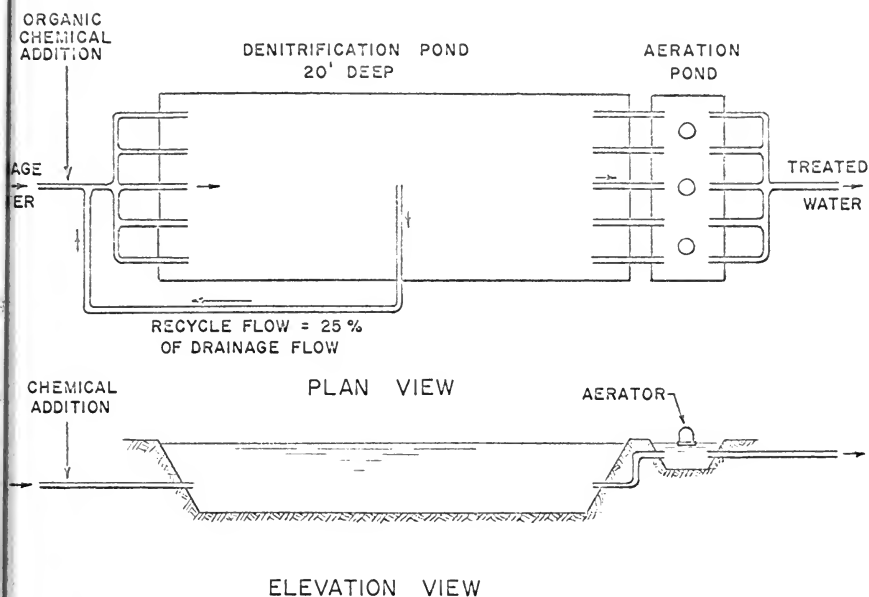


FIG. A-1. DIAGRAM OF DENITRIFICATION PROCESS FOR
TREATMENT OF AGRICULTURAL DRAINAGE WATER

time of about 10 days. During this treatment, the dissolved oxygen concentration of the drainage water will be reduced to zero. In order to prevent any harmful effect this may have on the receiving water, the denitrified water is aerated after it leaves the reservoir, but before it is discharged to the receiving water.

TABLE A-1

COSTS OF DIFFERENT CHEMICALS AND REQUIREMENTS FOR
DENITRIFICATION OF DRAINAGE WATER CONTAINING 21 MG/L
OF NITRATE NITROGEN AND 8 MG/L OF DISSOLVED OXYGEN

<u>Chemical</u>	Oxygen Equivalent in Pounds per <u>Pound of Chemical</u>	Concentration <u>Required</u>	Cost		
			<u>Per Pound of Chemical</u>	<u>Per Pound of Oxygen Equivalent</u>	<u>Per Million Gallons Treated</u>
Acetic Acid	1.07	87 mg/l	10.0 cents	9.3 cents	\$72.60
Acetone	2.21	42 "	6.6 "	3.0 "	\$23.20
Ethanol	2.08	45 "	9.0 "	4.3 "	\$33.80
Methanol	1.50	62 "	4.5 "	3.0 "	\$23.20
Sugar	1.07	87 "	9.2 "	8.6 "	\$66.70

In order for denitrification to proceed rapidly, a high concentration of denitrifying bacteria must be added to the water before it enters the reservoir. This is provided by the recycled flow shown in the diagram. A recycle flow rate equal to about 25 percent of the incoming flow rate is taken from the center of the reservoir and near the bottom. A relatively high concentration of denitrifying microorganisms should be present at this location. This recycled flow is continuously mixed with the drainage water before it enters the reservoir.

Denitrification can proceed only in the absence of oxygen. Some oxygen will enter through the open surface of the reservoir. However, it is believed that if the reservoir is sufficiently deep, any effect from this will be minimized. In addition, the maintenance of zero dissolved oxygen throughout the detention period will be enhanced if the influent and effluent pipelines are located below the midpoint of the reservoir.

The reservoirs should be designed to prevent short-circuiting of the drainage water through the basin. Thus, a good inlet and exit design will be required to allow even inlet and exit distribution. A relatively long and narrow tank will also help to minimize short-circuiting.

Estimated Treatment Costs

An economic evaluation of the denitrification process was based upon cost figures developed in a report on the "Removal of Pesticides and Algal Growth Potential from San Joaquin Valley Drainage Waters," by William J. Oswald, Donald G. Crosby, and Clarence G. Golueke. This report evaluated an alternate process for the treatment of the drainage waters. Use of the cost figures from this report allowed estimation of the cost of the denitrification process on a more comparable basis.

During the peak year in 1995, the drainage waters to be conveyed are estimated at 700 million gallons per day. To treat this quantity of water in 20 feet deep reservoirs with a ten day detention time would require reservoirs with a total surface area of approximately 1100 acres. The construction cost for these reservoirs should about equal the construction cost of \$2650 per acre for the digestion ponds suggested in the report by Oswald, et al. A group of reservoirs operated in parallel should be used to provide greater flexibility in operation.

An additional item of capital cost is the mechanical equipment including aerators, recirculating pumps, and chemical feeders. The largest item here would be for aerators, and the total cost would be equal to about one million dollars. The total capital cost including an item for engineering and contingencies is estimated to be \$5.5 million. Assuming a combined depreciation and interest rate of 10 percent, the annual cost for capital equipment and construction would be \$550,000 per year.

The above costs, together with the estimated annual operating cost for the peak year are listed in Table A-2. Power costs are based on \$0.01 per kilowatt hour. The largest power item is for aeration of the denitrified water. Additional power for recycle would also be required.

TABLE A-2

ESTIMATED COST FOR DENITRIFICATION OF 700 MGD OF
DRAINAGE WATER CONTAINING 21 MG/L NITRATE NITROGEN

Capital Cost for Equipment and Construction

Land Development and Piping - 1100 acres at \$2650	\$2,900,000
Aerators	700,000
Pumps and Chemical Feeders	300,000
Distributors and Collectors	500,000
Total	\$4,400,000
Engineering and Contingencies - 25%	1,100,000
Total Capital Cost:	\$5,500,000

Estimated Annual Cost

Depreciation and Interest - 10% of capital cost	\$ 550,000
Power for Aerators and Pumps	150,000
Operation and Maintenance - \$100/acre	110,000
Chemicals (62 mg/l methanol)	\$6,000,000
Total Annual Cost:	\$6,810,000

Cost per Million Gallons Treated - \$26.60

As indicated in Table A-2, the most expensive item is the organic chemicals required for denitrification. The value shown in the table is based on the current price for methanol as listed in Table A-1. This cost is almost directly proportional to the nitrate nitrogen concentration in the drainage waters, and is based on an estimated concentration of 21 mg/l. If the actual

concentration were lower, or if less than 90 percent nitrogen removal would be required, then this cost can be reduced proportionately. Also, if a cheaper chemical than methanol can be found, then this cost can be reduced. Using the values from Table A-2, the process cost will be \$26.60 per million gallons, based on current dollar value.

Summary and Recommendations

The denitrification process for removal of nitrate nitrogen from the San Joaquin Valley agricultural drainage water is a technically feasible process for use. This process has many desirable features. One of the most significant is that denitrification is a complete process. No materials requiring further treatment and disposal are created. In addition, the capital cost is quite low. The major item of expense is the chemical cost which does not have to be paid until treatment is actually required. This is of importance when the time value of money is considered.

Although the principles of denitrification have been known for some time, there has been little practical use made of this process for the removal of nitrogen except in a few cases where it has been tried on a limited scale for municipal waste treatment. For this reason, engineering experience with the denitrification process is almost non-existent. Therefore, it is necessary that the process be operated at a reasonable scale in the field to substantiate the laboratory findings, to fully evaluate the design parameters selected, and to determine what limitations the process may have.

The major cost of this process is for organic chemicals. This cost may be significantly reduced if a cheaper chemical can be found. Such a chemical should be relatively free from nitrogen containing compounds, or else it would be of little value. Organic waste from industry is one possible source. Preliminary studies indicated waste paper is also a source of organic material which could possibly be used for denitrification. Studies on this and similar materials should be continued. Another possibility to reduce chemical cost is through the use of special "autotrophic" bacteria which can denitrify while converting elemental sulfur to sulfates. Such possibilities should be explored.

Another possibly significant future cost is for land. There are promising methods of biological treatment by which the detention time for denitrification could be reduced from the 10 days recommended to only a few hours. More equipment and a somewhat higher power cost would be required, and this would have to be balanced against the cost of the additional land required for the presently proposed process. This possibility should be explored.

In summary, the following is recommended:

1. A field scale study should be instigated to determine the proper design factors as well as the limitations of the denitrification process.
2. Additional laboratory experimentation coupled with a search for more inexpensive materials to help further reduce the cost of denitrification should be carried out.
3. If land costs prove to be an important consideration, additional study should be instigated to perfect a high rate denitrification process.

LABORATORY EVALUATION OF DENITRIFICATION PROCESS

The laboratory study reported here was conducted to evaluate the feasibility of the biological denitrification process for removal of nitrate nitrogen from the future San Joaquin Valley agricultural drainage waters. An experimental investigation was conducted to evaluate the optimum detention time for the denitrification process as well as to determine the quantity and type of organic chemical which would be most feasible for use for nitrogen removal. All studies were made using 20 gallons of a natural subsurface irrigation drainage water furnished by the California Department of Water Resources. The chemical characteristics of this water are listed in Table A-3 along with a comparison of the projected characteristics of the agricultural drainage water to be carried by the future San Joaquin Valley Master Drain. The characteristics of the two are quite similar.

TABLE A-3

AGRICULTURAL DRAINAGE WATER CHARACTERISTICS

	Drainage Water Used in the Study	Concentration - mg/l	
		Projected San Joaquin Valley Drainage Water	
		Initial	After 50 years Operation
Total Dissolved Solids	9300	5800	2500
Chlorides	760	2150	957
Alkalinity	320	148	90
Carbon			
Total	86	-	-
Organic	9	-	-
Nitrogen			
Nitrate - N	25	-	-
Nitrite - N	0.0	-	-
Ammonia - N	0.0	-	-
Organic - N	0.4	-	-
Total - N	25.4	21	21
pH	7.5	-	-

The first phase of this study was directed toward an evaluation of the quantity and type of chemical which would be most feasible for use for nitrogen removal. This was followed by the second phase of study which was conducted to determine the most appropriate detention time for the denitrification process. All studies were conducted in a controlled temperature room at 20° C (68° F).

Phase 1 - Type and Quantity of Chemical for Denitrification

The denitrification process makes use of microorganisms which, in the absence of oxygen, couple the oxidation of organic matter (used for energy and growth) with the reduction of nitrate and nitrite nitrogen to nitrogen gas. The nitrogen is thus eliminated from the waste water as a gas. Since agricultural drainage waters contain little organic matter, this must be added for denitrification to occur.

Several commercially available organic chemical compounds were evaluated in this study. Those used were selected because of their low cost, water solubility, and probable ease of biodegradability. The studies were conducted on a batch basis.

An appropriate quantity of each organic chemical along with a small quantity of settled sewage which served as a source of microorganisms, was mixed with drainage water. A two liter bottle was filled with this mixture and then was sealed to prevent contact with the air so that oxygen could not enter the sample. This is a necessary condition for the denitrification process.

After appropriate time intervals, small samples were removed for analysis to determine the extent of the nitrogen removal obtained. Routine analyses were for nitrate nitrogen, nitrite nitrogen, pH, and soluble organic carbon. The latter analysis was conducted to evaluate the quantity of added organic compound remaining. At the end of each study period, a complete nitrogen analysis, including that for ammonia and organic nitrogen was made so that all nitrogen conversions could be better evaluated.

Initial Studies

An initial study was made to evaluate the quantity of organic chemical required for effective denitrification. Sugar and acetic acid were the chemicals chosen for this first study. An initial estimate indicated 100 mg/l of sugar would be required for removal of 25 mg/l of nitrate nitrogen. Three drainage water samples were prepared by adding 75 mg/l, 100 mg/l, and 150 mg/l of sugar, respectively. In addition, a sample containing 100 mg/l of acetic acid was prepared. These samples were seeded with microorganisms and were incubated for two weeks, after which a complete nitrogen analysis was made.

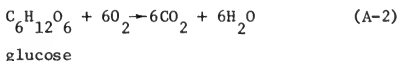
The results of this initial study confirmed that the estimated 100 mg/l both for sugar and for acetic acid were the appropriate quantities for use. When a smaller quantity of sugar was used, nitrogen removal was low. When a larger quantity was used, much organic material remained unused in solution.

Nitrogen removals obtained with acetic acid were superior to those obtained with sugar. The results also indicated that a large portion of nitrate nitrogen had been reduced to nitrite nitrogen as significant quantities of the latter were present after the incubation period.

Evaluation of Various Organic Compounds

The initial studies indicated that satisfactory prediction of the quantities of nitrate nitrogen from a waste can be evaluated from the oxygen equivalent (O_e) of the organic. The method for this prediction and use of this method for estimating the appropriate quantity of other organic chemicals is given below. This is followed by the results of an experimental evaluation of denitrification with various organic compounds.

The quantity of an organic compound required for removal of a given quantity of nitrate nitrogen from a waste can be evaluated from the oxygen equivalent (O_e) of the organic. The oxygen equivalent is the quantity of oxygen required for combustion of one pound of the organic to carbon dioxide and water. For example, with glucose sugar, the oxygen equivalent can be evaluated from the chemical equation for its combustion:



Thus, 1 mole of glucose requires 6 moles of oxygen for combustion, or 180 pounds of glucose would require 192 pounds of oxygen. Thus, the O_e of glucose is 192/180 or 1.07 pounds.

Theoretically, a quantity of organic waste with an O_e of 2.86 pounds would be required to convert one pound of nitrate nitrogen into nitrogen gas. However, in the biological process, about 25 percent of the added organic material is used by the microorganisms for cell synthesis and is therefore unavailable for denitrification. Thus, in practice, an organic waste with an O_e of 2.86/0.75 or 3.85 pounds is required per pound of nitrate nitrogen (NO_3-N). In addition, some organic material must be added to create the anaerobic conditions required for denitrification. This requires about 1.5 pounds of O_e per pound of dissolved oxygen (DO) in the incoming drainage water. In summary, the organic oxygen equivalent required (O_r) for denitrification can be evaluated as follows:

$$O_r = 3.85(NO_3-N) + 1.5(DO) \quad (A-3)$$

The organic compounds evaluated for denitrification of the agricultural drainage water, their oxygen equivalents and the quantity of each required for removal of 25 mg/l of nitrate nitrogen are listed in Table A-4. The organic oxygen equivalent required was evaluated from Eq. A-3 to be 108 mg/l. This number divided by the oxygen equivalent of the respective organic compounds gives the concentration of each chemical required as listed in the table. Sugar was not used in this study as its present market cost on an oxygen equivalent basis was higher than that of the four other compounds selected.

TABLE A-4

QUANTITY OF ORGANIC CHEMICALS REQUIRED FOR REMOVAL OF
25 MG/L NITRATE NITROGEN AND 8 MG/L DISSOLVED OXYGEN

<u>Chemical</u>	<u>Oxygen Equivalent - Pounds Oxygen per Pound Chemical</u>	<u>Concentration Required mg/l</u>
Sugar	1.07	101
Acetic Acid	1.07	101
Ethanol	2.08	52
Methanol	1.50	72
Acetone	2.21	49

The four compounds were added as in the initial studies and samples were taken periodically for nitrite and nitrate nitrogen analyses. The results are indicated in Figure A-2. The top graph shows the disappearance of nitrate nitrogen and indicates almost complete removal was obtained within 20 days in all units except the methanol unit. The middle graph, however, indicates that in most cases, the disappearance of nitrate nitrogen was accompanied by a build-up of nitrite nitrogen. Eventually, this too disappeared. The bottom graph is a combination of the upper two graphs and shows the disappearance of nitrite plus nitrate nitrogen. This graph gives a better indication of the overall nitrogen removal and indicates as in the initial study, that acetic acid is the most efficient chemical for use. However, in all cases, excellent nitrogen removal was eventually achieved. A summary of the analyses conducted after 42 days of incubation are shown in Table A-5. The results indicate that all compounds chosen

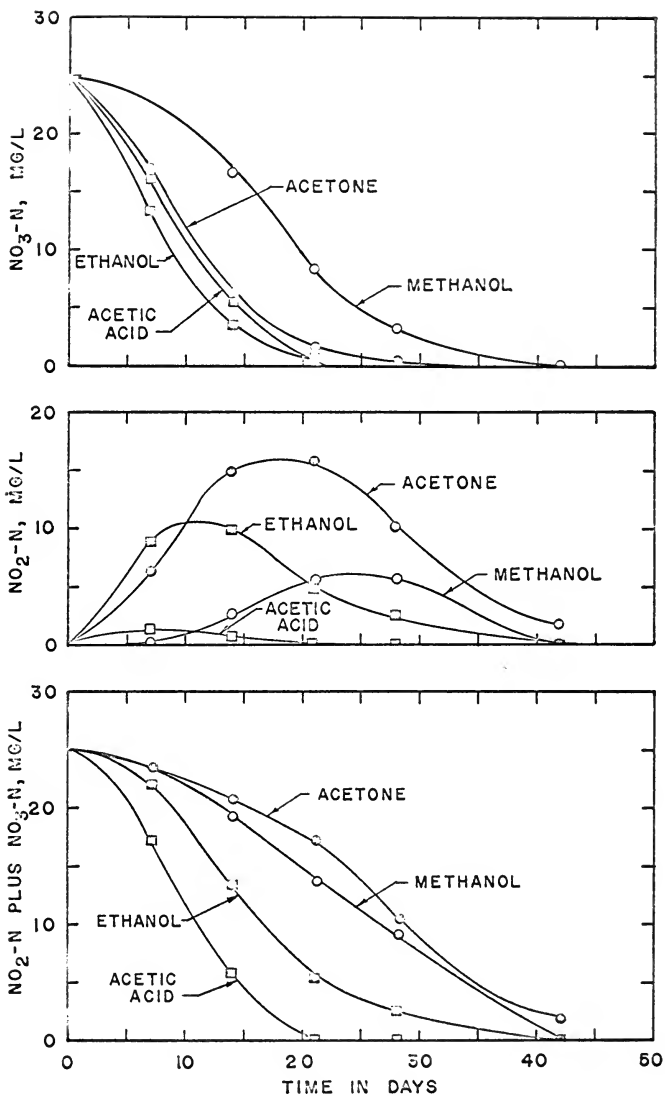


FIG. A-2. DENITRIFICATION WITH VARIOUS CHEMICALS

were satisfactory for denitrification, but to different degrees. In most cases, better than 90 percent nitrogen removal was obtained. Most of the remaining nitrogen was present as organic nitrogen, presumably as part of the biological cells synthesized during the process. The soluble organic carbon remaining in solution was only slightly over the 9 mg/l level of the raw waste water, indicating almost all of the added organic materials were consumed by the microorganisms. This was a further check on the correctness of the quantities added.

TABLE A-5

RESULTS OF DENITRIFICATION WITH VARIOUS ORGANIC
COMPOUNDS AFTER 42 DAYS OF INCUBATION

Treated Waste Characteristic	Organic Compound Added			
	Acetic Acid	Ethanol	Acetone	Methanol
Nitrogen - mg/l				
NO ₃ -N	0.0	0.1	0.2	0.0
NO ₂ -N	0.0	0.1	1.7	0.0
NH ₂ -N	0.0	0.0	0.2	0.1
Org-N	1.0	0.7	0.7	0.6
Total N	1.0	0.9	2.8	0.7
Nitrogen Removal - %	96	96	89	97
Soluble Organic Carbon-mg/l	12	11	13	11

The most efficient chemical indicated is acetic acid. However, on an oxygen equivalent basis, it is the most expensive of those tried. Methanol and acetone were the cheapest and about equivalent in cost. The overall results with methanol were somewhat better than with acetone. The methanol nitrite nitrogen buildup was smaller. Also, acetone is a somewhat volatile chemical and for this reason may not be a desirable chemical for field use. A second parallel study was conducted with methanol and confirmed the results of the study reported here. For these reasons, methanol was the chemical selected for further studies to determine an optimum detention time for continuous process operation.

Phase 2 - Detention Time Studies

The preceding studies were conducted on a batch basis to evaluate the various chemicals selected for denitrification. The denitrification process under field conditions, however, would best be a continuous process as described in the main body of this report. Before a field evaluation is made, it is desirable to have an idea of the detention times required for efficient denitrification under such continuous flow conditions and this was evaluated in this study.

Five bottles, each with a volume of approximately 1100 ml were used to hold the drainage water during treatment. Each bottle was fitted with appropriate stoppers and tubing so that waste could be removed and introduced each day with the introduction of as little air as possible into the bottle. Since methanol was the organic material selected for use in this study, a small quantity of bacteria developed in the methanol batch feed study was added to each of the bottles for seed. The bottles were then filled with agricultural drainage water to which 70 mg/l of methanol had been added.

Each day, the individual bottle contents were mixed and an appropriate quantity of the treated waste was removed. This was replaced with the same quantity of untreated drainage water containing 70 mg/l of methanol. The bottle contents were then mixed and allowed to stand until the following day when the procedure was repeated. This daily operation was continued for a total of 70 days.

The quantity of waste removed from three of the bottles was varied so that hydraulic detention times of 10, 20, and 30 days could be maintained, respectively. In two other bottles, hydraulic detention times of 20 days were also maintained. However, one bottle was stirred continuously to see if this would influence the denitrification process. The contents of the other 20 day bottle were not shaken prior to treated waste withdrawal. This allowed the withdrawal of a sample containing relatively little of the bacteria which was growing on the methanol added each day. The bacteria remained in the bottle and with time the bacterial mass present increased. It was desired to determine if this increased mass of bacteria would help speed up the denitrification process. As it turned out, the 20-day detention time bottle without these additional treatment procedures performed very well, and little difference between the efficiency of the three different 20 day detention time units was evident.

The average characteristics of the treated waste from the normally treated 10, 20, and 30 day detention time units are listed in Table A-6. The results indicate that even with the lowest detention time of 10 days, over 90 percent nitrogen removal was obtained. Efficient treatment at the short detention time was possible because continuous operation does not require the long period for biological adaptation as needed in the previous batch tests. The remaining soluble organic carbon was just slightly over the 9 mg/l present in the untreated drainage water, indicating little of the added methanol remained.

TABLE A-6
CHARACTERISTICS OF AGRICULTURAL DRAINAGE
WATERS AFTER CONTINUOUS TREATMENT AT
DIFFERENT HYDRAULIC DETENTION TIMES

	<u>Detention time - Days</u>		
	<u>10</u>	<u>20</u>	<u>30</u>
Nitrogen - mg/l			
NO ₃ -N	0.6	0.2	0.4
NO ₂ -N	0.2	0.4	0.2
NH ₄ ⁺ -N	0.1	0.0	0.0
Org-N	0.9	0.9	1.0
Total-N	1.8	1.5	1.6
Nitrogen Removal - %	93	94	94
Soluble Organic Carbon - mg/l	10	10	10
Volatile Suspended Solids - mg/l	36	44	24
BOD - mg/l	5	5	5
pH	7.9	8.1	8.1

The main adverse characteristic of the treated drainage water was the production of about 30 mg/l of organic suspended solids, which were presumed to be bacteria. This resulted in a small amount of turbidity in the treated drainage water. An analysis for biochemical oxygen demand (BOD) of

the treated water indicated a low value of about 5 mg/l. This probably resulted from the degradation of the bacteria which were present in the treated effluent. Although the treated water BOD is higher than that of the untreated water, it should still be sufficiently low so that it will cause little pollutional problems in receiving waters. Another characteristic of the treated water is that it would have a dissolved oxygen concentration of zero. It would be desirable to aerate the treated effluent to near oxygen saturation to prevent any detrimental effects this may have on receiving waters.

SUMMARY

Many organic chemicals can be used for the removal of nitrogen from agricultural drainage waters by the denitrification process. The cheapest and most satisfactory commercial chemical found for this purpose was methanol. The addition of 70 mg/l of this chemical to a typical agricultural drainage water containing 25 mg/l of nitrate nitrogen resulted in the removal of over 90 percent of the nitrogen containing compounds in the water, when detention times of 10 days or more were used. While satisfactory removal may be obtained at lower detention times, it is felt that a 10 day detention time should be used for full scale operation both as an added safety factor and also because efficiency would probably be lower at temperatures lower than the 20° C used for this study. It is highly probable that cheaper organic chemicals than methanol could be found for this process. Perhaps the cheapest compounds could be found among the many organic wastes produced by industry.

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